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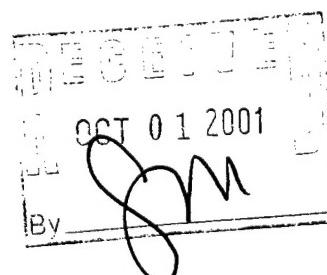
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13. ABSTRACT (Maximum 200 words) The goal of this project was to study the kinetics of fundamental free radical and ionic reactions in supercritical water (SCW). The first finding is that true diffusion controlled reactions are not impeded or enhanced by density inhomogeneities. This is based on a study of anthracene triplet-triplet annihilation in SCW at temperatures to 450°C. A second finding, based on a study of the reaction of xanthenium cations with amylamine, is that the rates of ion-neutral reactions in subcritical water follow simple Arrhenius behavior and can be easily extrapolated from ambient temperature measurements. The third finding is that the rate of hydroxyl radical addition to an aromatic ring in subcritical and supercritical water is well below the diffusion controlled limit and it is decidedly non-Arrhenius, with a rapid increase at temperatures above 300°C. This was determined by a pulse radiolysis study of the addition of hydroxyl radical to nitrobenzene at 250 bar and temperatures between 25°C and 390°C. We have been able to model this unusual behavior with a three-step mechanism that successfully predicts the rapid increase in the rate at supercritical temperatures. These studies provide fundamental kinetics upon which one can base modeling of supercritical water oxidation processes with elementary reactions.			
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Studies of Ionic and Free Radical Reactions in Supercritical Water

DAAG55-97-1-0025
Final Progress Report
4/1/97-3/31/01

Statement of Problem Studied

The United States Army is currently investigating the use of supercritical water oxidation (SCWO) for the destruction of stockpiled chemical weapons, including those stored in ton containers and those present in assembled chemical weapons. For instance, SCWO is currently the primary option for the destruction of VX hydrolysate at the facility in Newport, IN. In scientific support of these activities, the goal of this project was to study the kinetics of fundamental free radical and ionic reactions in supercritical water (SCW). Since numerous reactions occur during SCWO of even a single compound, it is difficult to develop an understanding of the temperature and pressure effect on individual reactions. The strategy taken in this study was to carefully isolate specific reactions so that the supercritical solvent effect on the reactions could be investigated in detail. Two tools, laser flash photolysis and pulse radiolysis, were exploited to perform these investigations.

Summary of Most Important Results

Three major scientific findings resulted from this project. The first finding is that true diffusion controlled reactions occur at the expected diffusion controlled limit in supercritical water. They are not impeded or enhanced by density inhomogeneities that may be present in the fluid. This is based on a study of anthracene triplet-triplet annihilation in SCW at temperatures to 450°C. A second finding is that the rates of ion-neutral reactions in subcritical water follow simple Arrhenius behavior and can be easily extrapolated from ambient temperature measurements. This is based on a study of the reactions of xanthenium cation and 9-phenylxanthenium cation with amyamine, a neutral nucleophile, in subcritical water to temperatures of 300°C. The third primary finding is that the rate of hydroxyl radical addition to an aromatic ring is well below the diffusion controlled limit and it is decidedly non-Arrhenius. The rates are essentially constant at temperatures below 300°C, but rise rapidly above this temperature, through the supercritical region. This was determined by a pulse radiolysis study of the addition of hydroxyl radical to nitrobenzene at 250 bar and temperatures between 25°C and 390°C. We have been able to model this unusual behavior with a three-step mechanism that successfully predicts the rapid increase in the rate at supercritical temperatures. These studies provide fundamental kinetics upon which one can base modeling of supercritical water oxidation processes with elementary reactions. The studies upon which each of these three findings are based, along with supporting work in the development of the high-temperature, high-pressure optical cell apparatuses and in lower temperature supercritical fluids, is described briefly below.

1. Anthracene Triplet-Triplet Annihilation

The triplet-triplet annihilation reaction of anthracene in supercritical water at temperatures between 375 and 450°C and pressures from 50 to 350 bar was studied to elucidate the effects of the supercritical water environment on a reaction that is known to be diffusion-controlled in most liquids. Observed rate constant and anthracene triplet extinction coefficient data were taken in order to determine the bimolecular rate constants as a function of temperature and pressure. Bimolecular rate constants were calculated at four isotherms and compared to the predicted diffusion-controlled values. The results at all temperatures are shown in Figure 1 and a comparison to the predicted diffusion-controlled values are shown for 420°C in Figure 2. The reaction rates occur just slightly above the diffusion-controlled limit predicted by the Stokes-Einstein based Debye equation, when the appropriate spin statistical factors are taken into account. Therefore, there is no evidence that this reaction is influenced by enhanced solute/solvent interactions and any effect of solute/solute interactions is small. Moreover, the mechanism of the reaction appears to be the same as it is in nonpolar liquid solvents. In general, this work corroborates the findings of studies of benzophenone TTA in lower temperature SCFs that concluded that these reactions occur at the diffusion-controlled limit that can be calculated from bulk viscosities.

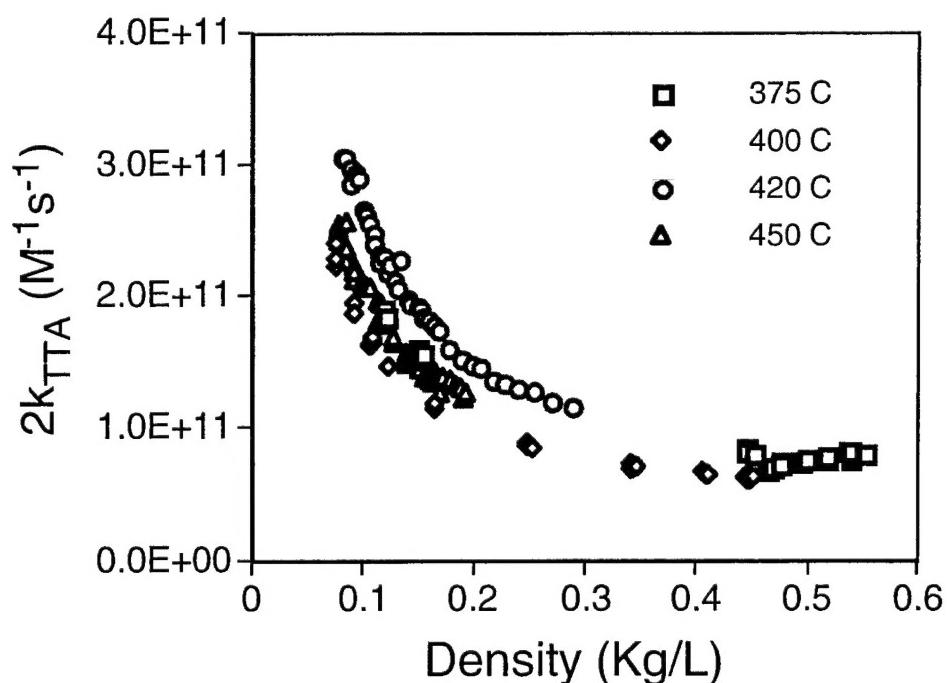


Figure 1 Experimental bimolecular rate constants, $2k_{\text{TTA}}$, for anthracene triplet-triplet annihilation in SCW at 375, 400, 420 and 450°C.

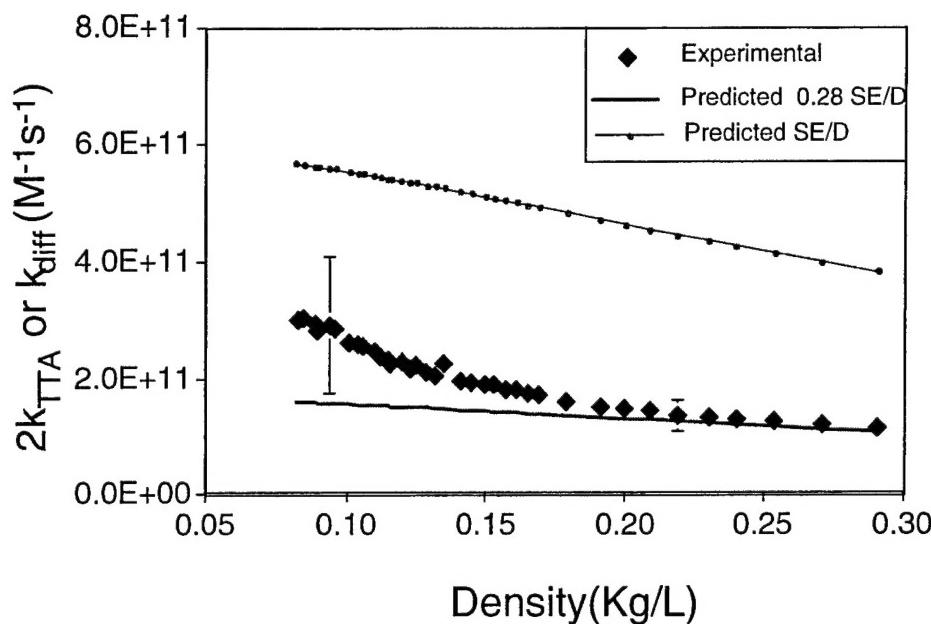


Figure 2 Experimental $2k_{TTA}$ and k_{diff} predicted by 0.28 SE/D and SE/D at 420°C as a function of density.

2. Reactions of Xanthenium Cations with Amylamine

Laser flash photolysis was used to generate 9-R-xanthenium cations ($R = H$ and C_6H_5) in sub-critical water to demonstrate the importance of ionic chemistry at these conditions. The carbocations were generated at temperatures up to 330 °C, but at higher temperatures the decrease in the dielectric constant of water resulted in weak cation signals with short lifetimes. Nonetheless, we determined that the temperature effect on the intrinsic solvent decay followed Arrhenius behavior and could be safely extrapolated all the way from ambient conditions to 300°C. In addition, we determined the bimolecular rate constants for the reactions of xanthenium and 9-phenylxanthenium cations with amylamine at temperatures between 100 °C and 300 °C. These ion/neutral isocoulombic reactions followed Arrhenius behavior according to $k_{bi} (M^{-1} s^{-1}) = 1.67 \pm 0.62 \times 10^{11} \exp [(-21.6 \pm 1.2 \text{ kJ mol}^{-1})/RT]$ and $k_{bi} (M^{-1} s^{-1}) = 5.39 \pm 3.25 \times 10^8 \exp [(-18.2 \pm 3.9 \text{ kJ mol}^{-1})/RT]$ for the 9-H-xanthen-9-ol and 9-phenylxanthen-9-ol systems, respectively. Moreover, these rate expressions predict the rate constants at ambient conditions extremely well. Thus, we conclude that for this kind of ion/neutral isocoulombic reaction it would be reasonable to use low temperature Arrhenius parameters to predict the rate constants in water at higher temperatures. Finally, we determined that there is no measurable pressure effect on the rate constants since water is still relatively incompressible at temperatures below 300 °C.

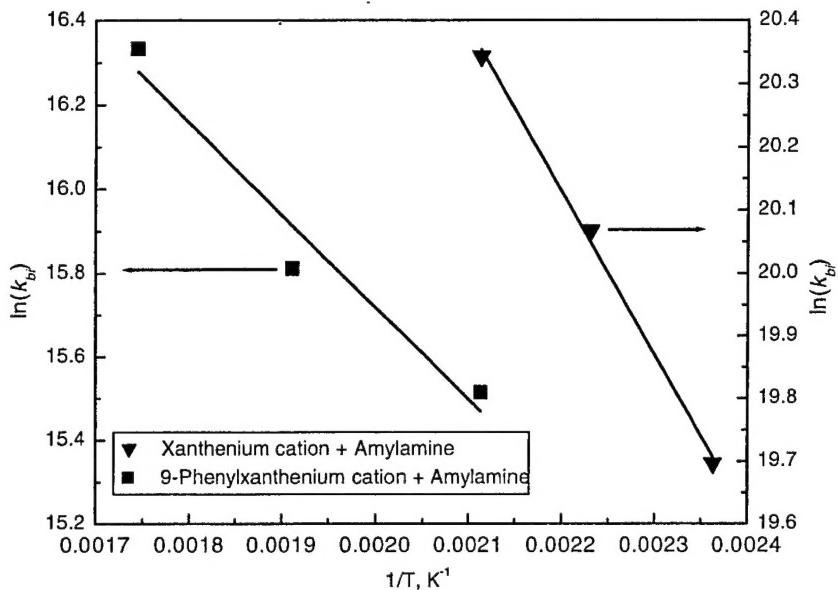


Figure 3 Arrhenius plot the bimolecular rate constant for the reaction between 9-R-xanthenium cation ($R = H$ and C_6H_5) and amyłamine at 230 bar.

3. Hydroxyl Radical Addition to Nitrobenzene

We have measured the bimolecular rate constants for the addition reaction of $^{\bullet}\text{OH}$ to $C_6H_5\text{NO}_2$ in water at temperatures between ambient and 390°C and at a pressure of 250 bar. $^{\bullet}\text{OH}$ was generated using pulse radiolysis and the kinetics determined by monitoring the growth of the nitrohydroxycyclohexadienyl radical. These are the first direct measurements of hydroxyl radical reactivity in supercritical water, which is important because the hydroxyl radical has been identified as one of the primary oxidizing species in supercritical water oxidation. These measurements can be used to evaluate and refine detailed SCWO models, which frequently use rate constants extrapolated directly from the combustion literature. Thus, important adjustments in the SCWO models can be performed, guided by this and further experimental work on individual reactions in SCW.

The measured bimolecular rate constants showed non-Arrhenius temperature dependence from ambient to 300°C, but increase dramatically at slightly subcritical and supercritical conditions (350 to 390°C, 250 bar). A three-step reaction mechanism including the formation of a π -complex intermediate as the precursor of the nitrohydroxycyclohexadienyl radical, proposed by Ashton et al. (Ashton, L.; Buxton, G. V.; Stuart, C. R. *J. Chem. Soc.-Faraday Trans.* **1995**, *91*, 1631-1633), was introduced to model the experimental results. This mechanism, using parameters determined from the lower temperature measurements (below 300°C), is able to model the bimolecular rate constants for the addition of $^{\bullet}\text{OH}$ to $C_6H_5\text{NO}_2$ at conditions through the supercritical region if accurate values of the species diffusion coefficients are available. However, the calculated k_{bi} depend heavily on the model chosen to estimate the diffusion coefficients of the hydroxyl radical. The experimental results, as well as the model, are shown in Figure 4.

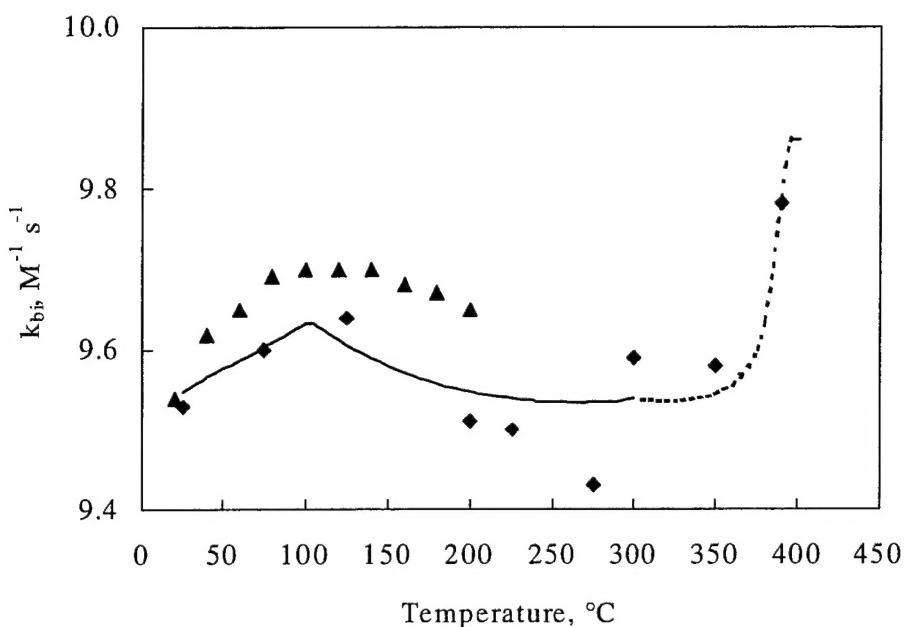


Figure 4. Comparison between the current experimental, Ashton et al. (Ashton, L.; Buxton, G. V.; Stuart, C. R. *J. Chem. Soc.-Faraday Trans.* **1995**, *91*, 1631-1633), and modeled bimolecular rate constants, k_{bp} , for the reaction between hydroxyl radical and nitrobenzene at 250 bar and temperatures between 25 and 390 °C. The solid line is the model result fitted from experimental values between 25 and 300 °C. The dotted line is the predicted bimolecular rate constants, k_{bp} , at temperatures between 300 and 390 °C, obtained by using the Arrhenius parameters determined at lower temperatures.

4. Supporting Work

In order to perform the experiments described above, we first had to develop and test a high-temperature, high-pressure optical cell that was suited for both laser flash photolysis and pulse radiolysis experiments. This cell was described in detail in the progress report for 4/1/97-12/31/97. This same cell was used in a static mode for the anthracene triplet-triplet annihilation experiments, as well as in a flow mode for the carbocation and hydroxyl radical reactivity experiments. The experimental details are described in the respective publications.

Also in support of the high temperature supercritical water work, we performed a study of electron transfer reactions in supercritical CO₂ and supercritical ethane. Specifically, we studied electron transfer reactivity of benzophenone triplet with triethylamine and 1,4-diazabicyclo[2.2.2]octane (DABCO). In liquids, these reactions occur at the diffusion control limit. In supercritical fluids, the rate constants are larger at lower pressures, where the solution is less viscous. However, the absolute values of the rate constants in supercritical fluids are well below the diffusion control limit, as predicted from the Stokes-Einstein based Debye equation (SE/D). The values of the rate constants are close to SE/D in liquids but over an order of magnitude below SE/D in SCFs. In fact, the bimolecular rate constants in SCFs at high pressures are very similar to the values in liquid solvents, even though the SCFs have much lower viscosities. Thus, electron transfer from amines to benzophenone triplet does not occur at the diffusion-controlled limit in SCFs. We believe this is a case in which the reaction actually has an

activation barrier, which is not readily apparent in liquids, but becomes obvious when running the reactions in the lower viscosity SCFs.

Publications Resulting from this Grant

(a) *Papers in Peer Reviewed Journals*

Daniel P. Roek, Mary J. Kremer, John E. Chateauneuf and Joan F. Brennecke, "Spectroscopic Studies of Solvent Effects on Reactions in Supercritical Fluids," Fluid Phase Equilibria, 158-160, 1999, p. 713-722.

Mary J. Kremer, Karen A. Connery, Matthew M. DiPippo, Junbo Feng, John E. Chateauneuf and Joan F. Brennecke, "Laser Flash Photolysis Investigation of the Triplet-Triplet Annihilation of Anthracene in Supercritical Water," J. Phys. Chem. A, 103(33), 1999, p. 6591-6598.

Sudhir N.V.K.Aki, Junbo Feng, John E. Chateauneuf and Joan F. Brennecke, "Generation of Xanthenium and 9-Phenylxanthenium Carbocations in Sub-critical Water and Reactivity with Amylamine," J. Phys. Chem.A, 105(34); 2001, p. 8046-8052.

(b) *Conference Proceedings*

Mary J. Kremer, Karen A. Connery, Matthew M. DiPippo, Junbo Feng, John E. Chateauneuf and Joan F. Brennecke, "Spectroscopy to Measure Solvation, Kinetics, and Equilibrium in Supercritical Fluids," Proceedings of the 6th Meeting on Supercritical Fluids: Chemistry and Materials, Nottingham, UK, April 10-13, 1999.

(c) *Meeting Presentations*

1. Joan F. Brennecke, "Electron-Transfer Reactions of Triplet Benzophenone with Amines in Supercritical Ethane and Carbon Dioxide," Argonne National Laboratory, December 16, 1997.
2. Joan F. Brennecke, "Solvent Effects on Near-Diffusion Controlled Reactions in Supercritical Fluids," Department of Chemistry, University of Utah, February 2, 1998.
3. John E. Chateauneuf and H. Jin, "Spectroscopic and Kinetic Investigations of Carbocation Reactivity in Supercritical Carbon Dioxide," 215th American Chemical Society National Meeting, Dallas, TX, March 29, 1998.
4. Joan F. Brennecke, Daniel P. Roek, Mary J. Kremer, and John E. Chateauneuf, "Solvent Effects on Energy and Electron Transfer in Supercritical Fluids," 215th American Chemical Society National Meeting, Dallas, TX, March 29, 1998.
5. Daniel P. Roek, Mary J. Kremer, John E. Chateauneuf, and Joan F. Brennecke, "Spectroscopic Studies of Solvent Effects on Reactions in Supercritical Fluids," Eighth International Conference on Properties and Phase Equilibria for Product and Process Design, Noordwijkerhout, The Netherlands, April 26 - May 1, 1998.
6. Joan F. Brennecke, "Energy and Electron Transfer Reactions as Probes of Local Environments in Supercritical Fluids," Department of Chemistry, University of Texas at Austin, Austin, TX, September 8, 1998.

7. Matthew M. DiPippo, Mary J. Kremer, Karen A. Connery, Joan F. Brennecke and John E. Chateauneuf, "Diffusion-Controlled and Ionic Reactivity in Supercritical Water," Annual AIChE Meeting, Miami, FL, November 15-20, 1998.
8. Joan F. Brennecke, Plenary Lecture, "Spectroscopy to Measure Solvation, Kinetics, and Equilibrium in Supercritical Fluids," 6th Meeting on Supercritical Fluids: Chemistry and Materials, Nottingham, UK, April 10-13, 1999.
9. John E. Chateauneuf and Joan F. Brennecke, "The Use of Reaction Intermediates to Probe Supercritical Fluid Solvent Effects," ACS National Meeting, New Orleans, August 22-26, 1999.
10. Sudhir N. V. K. Aki, John E. Chateauneuf, and Joan F. Brennecke, "In-situ Spectroscopic Investigation of Ionic Reactions in Sub and Supercritical Water," Annual AIChE Meeting, Dallas, TX, October 31 – November 5, 1999.
11. Kan Nie and John E. Chateauneuf, "Friedal-Crafts Reactions in Supercritical CO₂," Annual ACS Meeting, New Orleans, LA, March 26-30, 2000.
12. Joan F. Brennecke, "Spectroscopy in Sub- and Supercritical Fluids – Much More than an Analytical Tool," Keynote Address, Fifth International Symposium on Supercritical Fluids, Atlanta, GA, April 8-12, 2000.
13. Joan F. Brennecke, "Solvent Effects in Supercritical Fluid Reactions," Invited Seminar, Symposium on Fundamental Analysis and Design of Reaction and Separation Processes in Supercritical Fluids, University of Tokyo, October 4, 2000.
14. Junbo Feng, Sudhir N.V.K. Aki, Joan F. Brennecke, and John E. Chateauneuf, "Measurements of Hydroxyl Radical Reactivity in Supercritical Water Using Pulse Radiolysis," AIChE Annual Meeting, Los Angeles, CA, Nov. 12-17, 2000.
15. "Spectroscopy to Understand Solvation and Kinetics in Supercritical Fluids," 221st ACS National Meeting, Ipatieff Prize Lecture, San Diego, CA, April 1-5, 2001.
16. Sudhir N. V. K. Aki, Junbo Feng, John E. Chateauneuf, and Joan F. Brennecke, "Reactivity of Hydroxyl Radicals in Supercritical Water: A Pulse Radiolysis Study," (poster presentation) 221st ACS National Meeting, San Diego, CA, April 1-5, 2001.
17. Sudhir N. V. K. Aki, Junbo Feng, John E. Chateauneuf, and Joan F. Brennecke, "Generation of Xanthenium and 9-Phenylxanthenium Carbocations in Sub-critical Water and Reactivity with Amylamine," ACS Regional Meeting, Grand Rapids, MI, June 10-12, 2001.

(d) *Manuscripts Submitted*

Junbo Feng, Sudhir N.V.K. Aki, John E. Chateauneuf and Joan F. Brennecke, "Hydroxyl Radical Reactivity with Nitrobenzene in Subcritical and Supercritical Water," submitted to J. Am.Chem.Soc., 2001.

List of Scientific Personnel

The following personnel were involved with this project.

University of Notre Dame

Professor Joan F. Brennecke, Principal Investigator. She was awarded the 2001 Ipatieff Prize from the American Chemical Society in recognition of her research in supercritical fluid

technology. This is an award given once every three years to either a chemist or a chemical engineer under the age of 40 whose research is in either catalysis or high pressure.

Dr. Karen A. Connery, graduate student. Dr. Karen A. Connery successfully defended her Ph.D. degree in November, 1997 and is currently employed by Praxair.

Ms. Mary J. Kremer, graduate student. Ms. Kremer began her graduate studies at Notre Dame in Fall, 1996. She successfully defended her M.S. thesis on this work in December, 1998.

Mr. Junbo Feng, graduate student. Mr. Feng began his studies at Notre Dame in Fall, 1997 and successfully passed his Ph.D. candidacy exam in January, 2000. He anticipates completing his thesis in May, 2002.

Dr. Matthew DiPippo, Post-Doctoral Research Associate. Dr. DiPippo joined our group on Nov. 1, 1997, after completing his Ph.D. at the Massachusetts Institute of Technology, working in the group of Professor Jefferson Tester. He continued working on this project at the University of Notre Dame until October 31, 1998, when he assumed a position at Exxon in Houston, TX.

Dr. Sudhir Aki, Post-Doctoral Research Associate. Dr. Aki joined our group in November, 1998, after completing his Ph.D. in Chemical Engineering at the University of Toledo, working with Professor Martin Abraham. He has recently been appointed as a Research Assistant Professor at the University of Notre Dame.

Western Michigan University (subcontract)

Professor John E. Chateauneuf, Principal Investigator

Mr. Kan Nie, graduate student. Mr. Nie began his graduate studies at Western Michigan University in Fall, 1998 and defended his M.S. thesis in March, 2001.

Ms. H. Jin, graduate student. Ms. Jin began her graduate studies at Western Michigan University in Fall, 1996 and defended her thesis in 1998.

Inventions

There are no inventions to report for this grant.